



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08J 5/10, C08K 3/34, C08L 77/00	A1	(11) International Publication Number: WO 99/41299 (43) International Publication Date: 19 August 1999 (19.08.99)
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(54) Title: POLYMER NANOCOMPOSITE COMPOSITION		
(57) Abstract A polymer nanocomposite composition of a polyamide and a treated silicate, wherein the treated silicate includes a silicate material treated with at least one ammonium ion of the formula: $^+NR_1R_2R_3R_4$ wherein R_1 , R_2 , R_3 and R_4 are independently selected from a group consisting of a saturated or unsaturated C_1 to C_{22} hydrocarbon, substituted hydrocarbon and branched hydrocarbon, or where R_1 and R_2 form a N,N-cyclic ether, and optionally, one of R_1 , R_2 , R_3 and R_4 is hydrogen.		

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POLYMER NANOCOMPOSITE COMPOSITION

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Field of the Invention

This invention relates to a nanocomposite material comprising a polyamide matrix having dispersed therein a treated silicate. More particularly, this invention relates to a nanocomposite material having dispersed therein a silicate material treated with at least one ammonium ion.

Background of the Invention

International Application WO 93/04118 discloses a process of preparing a polymer nanocomposite having platelet particles dispersed therein. The process involves melt-processing the polymer with a swellable and polymer-compatible intercalated layered material and subjecting it to a shear rate sufficient to dissociate the layers. The layered material is compatibilized with one or more "effective swelling/compatibilizing agents" having a silane function or an onium cation function.

International Application WO 93/04117 discloses a process of preparing a polymer nanocomposite having platelet particles dispersed therein, where the polymer and the swellable and polymer-compatible intercalated layered material are melt-processed. The layered material is compatibilized with one or more "effective swelling/compatibilizing agents" selected from primary ammonium, secondary ammonium and quaternary phosphonium ions. The selected swelling/compatibilizing agents "...render their surfaces more organophilic than those compatibilized by tertiary and quaternary ammonium ion complexes...", facilitate exfoliation, resulting in less shear in mixing and less decomposition of the polymer, and heat stabilize the composite more than other cations (such as quaternary ammonium cation) swelling/compatibilizing agents.

International Patent Application WO 94/22430 discloses a nanocomposite composition having a polymer matrix comprising at least one gamma phase polyamide, and dispersed in the polyamide is a matrix of a nanometer-scale particulate material. The
5 addition of the particulate material to nylon 6 resulted in an improvement of flexural modulus and flexural strength (from 7 to 35%), when compared to unfilled nylon 6. The addition of the particulate material to nylon 6,6 resulted in very little improvement (1 to 3%) of flexural modulus and flexural strength
10 when compared to unfilled nylon 6,6.

International Patent Application WO 93/10098 discloses a polymer composite made by melt-processing a polymer with swellable and polymer-compatible intercalated layered material comprising layers having reactive organo- silane species
15 covalently bonded to their surfaces.

International Patent Application WO 95/14733 discloses a method of producing a polymer composite that does not demonstrate melting or glass transition by melt-processing a polymer with a layered gallery-containing crystalline silicate. The examples
20 include intercalated sodium silicate and a crystalline poly(ethylene oxide), montmorillonite intercalated with a quaternary ammonium and polystyrene, and montmorillonite intercalated with a quaternary ammonium and nylon 6.

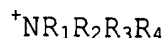
None of the above references, alone or in combination,
25 disclose the present invention, as claimed.

Summary of the Invention

This invention relates to a polymer nanocomposite composition suitable for automotive, electronic, film and fiber applications, where a combination of tensile strength, tensile
30 modulus and flexural modulus are required. Additionally, the claimed polymer nanocomposite composition also has a desirable surface appearance, toughness, ductility and dimensional

stability. The composition processes well and tolerates a wide range of molding conditions.

Such polymer nanocomposite composition comprises a polyamide and a treated silicate, wherein the treated silicate includes a silicate material treated with at least one ammonium ion of the formula:



wherein:

R_1 , R_2 , R_3 and R_4 are independently selected from a group consisting of a saturated or unsaturated C_1 to C_{22} hydrocarbon, substituted hydrocarbon and branched hydrocarbon, or where R_1 and R_2 form a N,N-cyclic ether. Examples include saturated or unsaturated alkyls, including alkylenes; substituted alkyls such as hydroxyalkyls, alkoxyalkyls, alkoxy, amino alkyls, acid alkyls, halogenated alkyls, sulfonated alkyls, nitrated alkyls and the like; branched alkyls; aryls and substituted aryls, such as alkylaryls, alkoxyaryls, alkylhydroxyaryls, alkylalkoxyaryls and the like. Optionally, one of R_1 , R_2 , R_3 and R_4 is hydrogen. The milligrams of treatment per 100 grams of silicate (MER) of the treated silicate, described in more detail below, is from about 10 milliequivalents/100 g below the cation exchange capacity of the untreated silicate to about 30 milliequivalents/100 g above the cation exchange capacity of the untreated silicate. The composite polymer matrix material demonstrates, when tested, an improvement in tensile modulus and flexural modulus, without a substantial decrease in tensile strength, when compared to that of the polymer without the treated silicate. As utilized herein, "substantial decrease" means a decrease exceeding the statistically determined deviations.

The present invention further relates to a process to prepare the above polymer nanocomposite composition comprising forming a flowable mixture of a polyamide and a treated silicate

material and dissociating (as that term is described in more detail below) at least about 50% but not all of the treated silicate. The treated silicate is a silicate material treated with at least one ammonium ion of the formula:



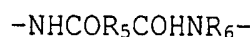
wherein:

R_1 , R_2 , R_3 and R_4 are independently selected from a group consisting of a saturated or unsaturated C_1 to C_{22} hydrocarbon, substituted hydrocarbon and branched hydrocarbon, or where R_1 and
10 R_2 form a N,N-cyclic ether. Examples include saturated or unsaturated alkyls, including alkylenes; substituted alkyls such as hydroxyalkyls, alkoxyalkyls, alkoxys, amino alkyls, acid alkyls, halogenated alkyls, sulfonated alkyls, nitrated alkyls and the like; branched alkyls; aryls and substituted aryls, such
15 as alkylaryls, alkoxyaryls, alkylhydroxyaryls, alkylalkoxyaryls and the like. Optionally, one of R_1 , R_2 , R_3 and R_4 is hydrogen. The milligrams of treatment per 100 grams of silicate (MER) of the treated silicate, described in more detail below, is from about 10 milliequivalents/100 g below the cation exchange
20 capacity of the untreated silicate to about 30 milliequivalents/100 g above the cation exchange capacity of the untreated silicate. The composite polymer matrix material demonstrates, when tested, an improvement in tensile modulus and flexural modulus, without a significant decrease in tensile
25 strength, when compared to that of the polymer without the treated silicate.

Description of the Preferred Embodiments
of the Invention

Polyamides of the present invention are synthetic linear
30 polycarbonamides characterized by the presence of recurring carbonamide groups as an integral part of the polymer chain which are separated from one another by at least two carbon atoms. Polyamides of this type include polymers, generally known in the

art as nylons, which can be obtained from diamines and dibasic acids having the recurring unit represented by the general formula:



5 in which R_5 is an alkylene group of at least 2 carbon atoms, preferably from about 2 to about 11 or arylene having at least about 6 carbon atoms, preferably about 6 to about 17 carbon atoms; and R_6 is selected from R_5 and aryl groups. Also, included are copolyamides, terpolyamides and the like obtained by
10 known methods, for example, by condensation of hexamethylene diamine and a mixture of dibasic acids consisting of terephthalic acid and adipic acid. Polyamides of the above description are well-known in the art and include, for example, poly(hexamethylene adipamide) (nylon 6,6), poly(hexamethylene sebacamide) (nylon 6,10), poly(hexamethylene isophthalamide),
15 poly(hexamethylene terephthalamide), poly(heptamethylene pimelamide) (nylon 7,7), poly(octamethylene suberamide) (nylon 8,8), poly(nonamethylene azelamide) (nylon 9,9), poly(decamethylene sebacamide) (nylon 10,9), poly(decamethylene sebacamide) (nylon 10,10), poly[bis(4-amino cyclohexyl)methane-1,10-decanecarboxamide], poly(m-xylene adipamide), poly(p-xylene sebacamide), poly(2,2,2-trimethyl hexamethylene terephthalamide), poly(piperazine sebacamide), poly(p-phenylene terephthalamide), poly(metaphenylene isophthalamide), and copolymers and
20 terpolymers of the above polymers. Additional polyamides include nylon 4,6, nylon 6,9, nylon 6,10, nylon 6,12, nylon 11, nylon 12, amorphous nylons, aromatic nylons and their copolymers.

Other useful polyamides are those formed by polymerization of amino acids and derivatives thereof, as for example, lactams.

30 Illustrative of these useful polyamides are poly(caprolactam) (nylon 6), poly(4-aminobutyric acid) (nylon 4), poly(7-aminoheptanoic acid) (nylon 7), poly(8-aminooctanoic acid) (nylon 8), poly(9-aminononanoic acid) (nylon 9), poly(10-aminodecanoic

acid) (nylon 10), poly(11-aminoundecanoic acid) (nylon 11), poly(12-aminododecanoic acid) (nylon 12) and the like.

The preferred polyamide is Vydyne® nylon, which is poly(hexamethylene adipamide) (nylon 6,6), which gives a composite with the desired combination of tensile strength, tensile modulus and flexural modulus for the applications contemplated herein (Vydyne® is a registered trademark of Solutia, Inc.).

The preferred molecular weight of the polyamide is in the range of 30,000 to 80,000 D (weight average) with a more preferred molecular weight of at least 40,000 D (weight average).

Increasing the weight average molecular weight of the polyamide from about 35,000 to 55,000 D results in an unexpected increase in toughness as indicated by the notched izod impact test.

Whereas an increase in the weight average molecular weight of from about 35,000 to 55,000 D in the polyamide neat results in a small increase in toughness, the same increase in molecular weight in the nanocomposite results about twice the increase in toughness. Therefore, the increase in toughness is enhanced in the nanocomposite when compared to that of the polyamide neat.

In a preferred embodiment, the polyamide has an amine end group/acid end group ratio greater than one (1). More preferably, the concentration of amine end groups is at least 10 mole % greater than the concentration of the carboxylic acid end groups. In an even more preferred embodiment, the polyamide has a concentration of amine end groups at least 20 mole % greater than the concentration of the carboxylic acid end groups, and in a most preferred embodiment, the polyamide has a concentration of amine end groups at least 30 mole % greater than the concentration of the carboxylic acid end groups. In another embodiment, the concentration of amine end groups is essentially equal to the concentration of carboxylic acid end groups.

Among the preferred embodiments is nylon 6, nylon 6,6, blends thereof and copolymers thereof. The range of ratios of the nylon 6/nylon 6,6 in the blends is from about 1/100 to 100/1.

Preferably, the range is from about 1/10 to 10/1. The range of ratios of the nylon 6/nylon 6,6 in the copolymers is about 1/100 to 100/1. Preferably, the range is from about 1/10 to 10/1.

Optionally, the nanocomposite composition comprises at least one additional polymer. Examples of suitable polymers include polyethyleneoxide, polycarbonate, polyethylene, polypropylene, poly(styrene-acrylonitrile), poly(acrylonitrile-butadiene-styrene), poly(ethylene terephthalate), poly(butylene terephthalate), poly(trimethylene terephthalate), poly(ethylene naphthalate), poly(ethylene terephthalate-co-cyclohexane dimethanol terephthalate), polysulphone, poly(phenylene oxide) or poly(phenylene ether), poly(hydroxybenzoic acid-co-ethylene terephthalate), poly(hydroxybenzoic acid-co-hydroxynaphthenic acid), poly(esteramide), poly(etherimide), poly(phenylene sulfide), poly(phenylene terephthalamide).

The mixture may include various optional components which are additives commonly employed with polymers. Such optional components include surfactants, nucleating agents, coupling agents, fillers, impact modifiers, chain extenders, plasticizers, compatibilizers, colorants, mold release lubricants, antistatic agents, pigments, fire retardants, and the like.

Suitable examples of fillers include carbon fiber, glass fiber, kaolin clay, wollastonite and talc. Suitable examples of compatibilizers include acid-modified hydrocarbon polymer, such as maleic anhydride-grafted propylethylene, maleic anhydride-grafted polypropylene, maleic anhydride-grafted ethylenebutylene-styrene block copolymer. Suitable examples of mold release lubricant includes alkyl amine, stearamide, and di-or tri-aluminum stearate.

Suitable examples of impact modifiers include ethylene-propylene rubber, ethylene-propylene diene rubber, methacrylate-butadiene-styrene (with core-shell morphology), poly(butylacrylate) with or without carboxyl modification, 5 poly(ethylene acrylate), poly(ethylene methacrylate), poly(ethylene acrylic acid), poly(ethylene acrylate) ionomers, poly(ethylene methacrylate acrylic acid) terpolymer, poly(styrene-butadiene)block copolymers, poly(styrene-butadiene-styrene)block terpolymers, poly(styrene-ethylene/butylene- 10 styrene) block terpolymers and poly(styrene-ethylene/butylene-styrene carboxylate) block terpolymers.

Silane coupling agents are well-known in the art and are useful in the present invention. Examples of suitable coupling agents include octadecyltrimethoxysilane, gamma- 15 aminopropyltriethoxysilane, gamma-aminopropyltrimethoxysilane, gamma-aminopropylphenyldimethoxysilane, gamma-glycidoxypropyl tripropoxysilane, 3,3-epoxycyclohexylethyl trimethoxysilane, gamma-propionamido trithoxysilane, N-trimethoxysilylpropyl-N(beta-aminoethyl) amine, trimethoxysilylundecylamine, 20 trimethoxysilyl-2-chloromethylphenylethane, trimethoxysilylethylphenylsulfonlazide, N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride, N-(trimethoxysilylpropyl)-N-methyl-N,N-diallylammonium chloride, trimethoxysilylpropylcinnamate, 3-mercaptopropyl 25 trimethoxysilane, 3-isocyanatopropyltriethoxysilane, and the like. The preferred silane is gamma-aminopropyltriethoxysilane.

The silane coupling agent is optionally added to the polymer composite in the range of about 0.5 to 5 weight % of the layered silicate. The preferred concentration range of silane coupling 30 agent is about 1 to 3 weight % of the layered silicate in the composite.

In one embodiment, the nanocomposite composition further comprises a composition wherein an acid end group of the

polyamide is bonded to a surface of the treated layered silicate by a silane coupling agent.

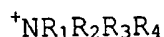
The silicate materials of the present invention are selected from the group consisting of layered silicates and fibrous, chain-like silicates, and include phyllosilicates. Examples of fibrous, chain-like silicates include chain-like minerals, for example sepiolite and attapulgite, with sepiolite being preferred. Such silicates are described, for example, in Japanese Patent Application Kokoku 6-84435 published October 26, 1994. Examples of layered silicates include layered smectite clay minerals such as montmorillonite, nontronite, beidellite, volkonskoite, Laponite® synthetic hectorite, natural hectorite, saponite, sauconite, magadiite, and kenyaite; vermiculite; and the like. Other useful materials include layered illite minerals such as ledikite and admixtures of illites with one or more of the clay minerals named above. The preferred layered silicates are the smectite clay minerals such as montmorillonite, nontronite, beidellite, volkonskoite, Laponite® synthetic hectorite, natural hectorite, saponite, sauconite, magadite, and kenyaite.

The layered silicate materials suitable for use in the present invention are well-known in the art, and are sometimes referred to as "swellable layered material". A further description of the claimed layered silicates and the platelets formed when melt processed with the polyamide is found in International Patent Application WO 93/04117, which is hereby incorporated by reference. The layered silicate materials typically have planar layers arrayed in a coherent, coplanar structure, where the bonding within the layers is stronger than the bonding between the layers such that the materials exhibit increased interlayer spacing when treated.

The layered silicate materials require treatment as described in more detail below with the subject ammonium ion to

provide the interlayer swelling and/or spacing required for the performance of the treated silicate of the present invention. As used herein the "inter layer spacing" refers to the distance between the faces of the layers as they are assembled in the treated material before any delamination (or exfoliation) takes place. The preferred clay materials generally include interlayer or exchangeable cations such as Li^+ , Na^+ , Ca^{+2} , K^+ , Mg^{+2} and the like. In this state, these materials have interlayer spacings usually equal to or less than about 4 Å and only delaminate to a low extent in host polymer melts regardless of mixing. In the claimed embodiments, the cationic treatment is an ammonium species which is capable of exchanging with the interlayer cations such as Li^+ , Na^+ , Ca^{+2} , K^+ , Mg^{+2} and the like in order to improve delamination of the layered silicate.

The treated silicate of the present invention is a silicate material as described above which is treated with at least one ammonium ion of the formula



wherein:

R_1 , R_2 , R_3 and R_4 are independently selected from a group consisting of a saturated or unsaturated C_1 to C_{22} hydrocarbon, substituted hydrocarbon and branched hydrocarbon, or where R_1 and R_2 form a N,N-cyclic ether. Examples include saturated or unsaturated alkyls, including alkylenes; substituted alkyls such as hydroxyalkyls, alkoxyalkyls, alkoxys, amino alkyls, acid alkyls, halogenated alkyls, sulfonated alkyls, nitrated alkyls and the like; branched alkyls; aryls and substituted aryls, such as alkylaryls, alkoxyaryls, alkylhydroxyaryls, alkylalkoxyaryls and the like. Optionally, one of R_1 , R_2 , R_3 and R_4 is hydrogen. A mixture of two or more ammonium ions is contemplated by the present invention.

In a preferred embodiment of the present invention, R_1 is selected from the group consisting of hydrogenated tallow,

unsaturated tallow or a hydrocarbon having at least 6 carbons, and R₂, R₃ and R₄ independently have from one to eighteen carbons.

Tallow is composed predominantly of octadecyl chains with small amounts of lower homologues, with an average of from 1 to 2
5 degrees of unsaturation. The approximate composition is 70% C₁₈, 25% C₁₆, 4% C₁₄ and 1% C₁₂. In another preferred embodiment of the present invention, R₁ and R₂ are independently selected from the group consisting of hydrogenated tallow, unsaturated tallow or a hydrocarbon having at least 6 carbons and R₃ and R₄ independently
10 have from one to twelve carbons.

Examples of suitable R₁, R₂, R₃ and R₄ groups are alkyl such as methyl, ethyl, octyl, nonyl, tert-butyl, ethylhexyl, neopentyl, isopropyl, sec-butyl, dodecyl and the like; alkenyl such as 1-propenyl, 1-butenyl, 1-pentenyl, 1-hexenyl, 1-heptenyl,
15 1-octenyl and the like; cycloalkyl such as cyclohexyl, cyclopentyl, cyclooctyl, cycloheptyl and the like; alkoxy such as ethoxy; hydroxyalkyl; alkoxyalkyl such as methoxymethyl, ethoxymethyl, butoxymethyl, propoxyethyl, pentoxybutyl and the like; aryloxyalkyl and aryloxyaryl such as phenoxyphenyl,
20 phenoxymethyl, phenoxydecyl, phenoxyoctyl and the like; arylalkyl such as benzyl, phenylethyl, 8-phenyloctyl, 10-phenyldecyl and the like, alkylaryl such as 3-decylphenyl, 4-octylphenyl, nonylphenyl and the like.

The preferred ammoniums used in treating the silicate
25 materials include oniums such as dimethyldi(hydrogenated tallow) ammonium, dimethylbenzyl hydrogenated tallow ammonium, dimethyl(ethylhexyl) hydrogenated tallow ammonium, trimethyl hydrogenated tallow ammonium, methylbenzyldi(hydrogenated tallow) ammonium, N,N-2-cyclobutoxydi(hydrogenated tallow) ammonium,
30 trimethyl tallow ammonium, methyldihydroxyethyl tallow ammonium, octadecylmethyldihydroxyethyl ammonium, dimethyl(ethylhexyl) hydrogenated tallow ammonium and mixtures thereof. Particularly preferred ammoniums include quaternary ammoniums, for example,

dimethyldi(hydrogenated tallow) ammonium, dimethylbenzyl
hydrogenated tallow ammonium, methyldihydroxyethyl tallow
ammonium, octadecylmethyldihydroxyethyl ammonium,
dimethyl(ethylhexyl) hydrogenated tallow ammonium and mixtures
5 thereof.

The treatment with the ammonium ion(s), also called
"cationic treatments", may include introduction of the ions into
the silicate material by ion exchange. In the embodiment where
the silicate material is a layered silicate, the cationic
10 treatments may be introduced into the spaces between every layer,
nearly every layer, or a large fraction of the layers of the
layered material such that the resulting platelet layers comprise
less than about 20 particles in thickness. The platelet layers
are preferably less than about 8 particles in thickness, more
15 preferably less than about 5 particles in thickness, and most
preferably, about 1 or 2 particles in thickness.

The treated silicate has a MER of from about 10
milliequivalents/100 g below the cation exchange capacity of the
untreated silicate to about 30 milliequivalents/100 g above the
20 cation exchange capacity of the untreated silicate. The MER is
the milliequivalents of treatment per 100 g of silicate. Each
untreated silicate has a cation exchange capacity, which is the
milliequivalents of cations available for exchange per 100 g of
silicate. For example, the cation exchange capacity of the
25 layered silicate montmorillonite can be about 95, and the
exchange capacity of sepiolite is in the range of about 25 to 40.

When the MER of the treated silicate substantially exceeds the
cation exchange capacity, there is an excess of cationic
treatment which may be available to react with the polyamide.
30 This excess may cause degradation of the properties of the
polyamide.

The higher the MER, the lower the concentration of
silicate in the treated silicate. Therefore, a first

nanocomposite sample may have a higher concentration of treated silicate but a lower concentration of silicate, than a second nanocomposite sample, because the first sample has a higher MER than the second sample.

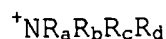
5 If the MER value of the treated silicate is substantially less than its exchange capacity, for example about 85 MER for the preferred montmorillonite, there is too little of the cationic treatment to have a beneficial effect. If the MER exceeds about 125, the excess ammonium may be detrimental to the properties of
10 the nylon. Preferably, when the untreated montmorillonite has an exchange capacity of 95, the treated layered silicate has a cation exchange capacity of from about 85 to about 125.

 The amount of treated silicate included in the composition is in the range of about 0.1 to 12 weight % of the composite.
15 The concentration is adjusted to provide a composite polymer matrix material which demonstrates, when tested, an increase in tensile modulus and flexural modulus, without a decrease in tensile strength. Preferably, the increase in tensile modulus and flexural modulus is at least about 10%. More preferably, the
20 increase in tensile modulus and flexural modulus is at least about 20%. Too little treated silicate fails to provide the desired increase in tensile modulus and flexural modulus. Too much treated silicate provides a polyamide composite with a decreased tensile strength. Further, it may be desirable to have
25 the crystalline regions of the polyamide in the nanocomposite composition be less than 1.0 μ m.

 The particle size of the treated silicate is such that optimal contact between the polymer and the treated silicate is facilitated. The range of particle size can vary from about 10
30 microns to about 100 microns. Preferably, the particle size is in the range of from about 20 to 80 microns. Most preferably, the particle size is below about 30 microns, such as those that

pass through 450 mesh screens, in that the resulting polymer nanocomposite has improved performance properties.

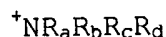
Optionally, the silicate can be treated with a mixture of one or more quaternary ammonium ions with one or more ammonium ions of the formula



wherein at least one of R_a , R_b and R_c is hydrogen (H) and R_d is selected from a group consisting of a saturated or unsaturated C_1 to C_{22} hydrocarbon, substituted hydrocarbon and branched

hydrocarbon. Examples include saturated or unsaturated alkyls, including alkylenes; substituted alkyls such as hydroxyalkyls, alkoxyalkyls, alkoxys, amino alkyls, acid alkyls, halogenated alkyls, sulfonated alkyls, nitrated alkyls and the like; branched alkyls; aryls and substituted aryls, such as alkylaryls, alkyoxyaryls, alkylhydroxyaryls, alkylalkoxyaryls and the like.

As the definition of the R_d group for the ammonium ion above is generally the same as the definition for the R_4 group in the ammonium ion, which in this embodiment is a quaternary ammonium, the Examples set forth above for the R_4 group are also exemplary of the R_d group. Optionally, the R_d group further contains a carboxylic acid moiety such that the ammonium ion



is an amino acid, for example 12-aminolauric acid ammonium. In this embodiment, it is particularly preferred that the amine end groups/acid end groups ratio of the polyamide is greater than one (1).

A preferred mixture includes at least one of dimethyldi(hydrogenated tallow) ammonium, methyl dihydroxyethyl tallow ammonium and/or dimethyl(ethylhexyl) hydrogenated tallow ammonium, either alone or in combination with 12-aminolauric acid ammonium.

Optionally, the treated silicate can be further treated with azine cationic dyes, such as nigrosines or anthracines.

Said cationic dyes would impart color-fastness and uniformity of color in addition to increasing the intercalation of the polymer molecules.

It is further desirable to have a polymer composite that provides both the desired strength and flexibility, and yet is lightweight. This is accomplished by minimizing the concentration of treated silicate in the nanocomposite. The preferred nanocomposite contains a concentration of treated silicate of from about 0.1 to about 12.0 weight % of the composite. The most preferred nanocomposite contains a concentration of treated silicate of from about 0.5 to about 6.0 weight % of the composite.

In a first embodiment of the present invention, the nanocomposite composition is prepared using a two step process. One step includes forming a flowable mixture of the polyamide as a polymer melt and the treated silicate material. The other step includes dissociating at least 50% but not all of the treated silicate material. The term "dissociating", as utilized herein, means delaminating or separating treated silicate material into submicron-scale structures comprising individual or small multiple units. For the embodiment wherein layered silicates are utilized this dissociating step includes delaminating the treated silicate material into submicron scale platelets comprising individual or small multiple layers. For the embodiment wherein fibrous, chain-like silicates are utilized, this dissociating step includes separating the treated silicate material into submicron scale fibrous structures comprising individual or small multiple units.

As referred to in the mixture forming step, a flowable mixture is a mixture which is capable of dispersing dissociated treated silicate material at the submicron scale. A polymer melt is a melt processable polymer or mixture of polymers which has been heated to a temperature sufficiently high to produce a

viscosity low enough for submicron scale mixing to occur. The process temperature should be at least as high as the melting point of the polyamide employed and below the degradation temperature of the polyamide and of the organic treatment of the silicate. The actual extruder temperature may be below the melting point of the polyamide employed, because heat is generated by the flow. The process temperature is high enough that the polymer will remain in the polymer melt during the conduct of the process. In the case of a crystalline polyamide, that temperature is above the polymer's melting temperature. For example, a typical nylon 6, having a melting point of about 225°C, can be melted in an extruder at any temperature equal to or greater than about 225°C, as for example between about 225°C and about 260°C. For nylon 6,6 a temperature of preferably from about 260°C to about 320°C is normally employed.

Conventional methods can be employed to form the flowable mixture. For example, the flowable mixture can be prepared through use of conventional polymer and additive blending means, in which the polymer is heated to a temperature sufficient to form a polymer melt and combined with the desired amount of the treated silicate material in a granulated or powdered form in a suitable mixer, as for example an extruder, a Banbury® type mixer, a Brabender® type mixer, Farrel® continuous mixers, and the like.

In one embodiment, the flowable mixture may be formed by mixing the polyamide with a previously formed treated silicate-containing concentrate. The concentrate includes the treated silicate and a polymer carrier. The concentration of the treated silicate material in the concentrate is selected to provide the desired treated silicate concentration for the final nanocomposite composition. Examples of suitable polymers for the carrier polymer of the concentrate include polyamide, ethylene propylene rubber, ethylene propylene diene rubber, ethylene-

ethylacrylate, ethylene-ethylmethacrylate or ethylene methacrylate. Examples include Iotek® ionomer and Escor® ATX acid terpolymer, both available from Exxon. The polyamide polymers suitable for the carrier polymer include nylons such as
5 nylon 6, nylon 6,6, nylon 4,6, nylon 6,9, nylon 6,10, nylon 6,12, nylon 11, nylon 12, amorphous nylons, aromatic nylons and their copolymers. The polymer of the carrier may be the same as or different from the polyamide of the flowable mixture. For example, both polymers may be a polyamide, particularly nylon
10 6,6, but may have the same or different molecular weight. The preferred weight average molecular weight of the carrier polymer of the concentrate is in the range of about 5,000 D to about 60,000 D. The most preferred range of the weight average molecular weight for the carrier polymer is in the range of about
15 10,000 to about 40,000 D. In this embodiment, the dissociation step of the present process, as described below, may occur at least in part via the forming of the concentrate such that the dissociation step may precede the step of forming the flowable mixture. It is therefore understood that the process steps
20 (e.g., forming and dissociating) may occur sequentially without regard to order, simultaneously or a combination thereof. In the second step, the flowable mixture is sufficiently mixed to form the dispersed nanocomposite structure of dissociated silicate in the polymer melt, and it is thereafter cooled. The
25 silicate can be dissociated by being subjected to a shear having an effective shear rate. As used herein, an effective shear rate is a shear rate which is effective to aid in dissociation of the silicate and provide a composition comprising a polyamide matrix having silicate substantially homogeneously dispersed therein
30 without substantially breaking the individual units (e.g., platelets or fibrous chains).

Any method which can be used to apply a shear to a flowable mixture or any polymer melt can be used. The shearing

action can be provided by any appropriate method, such as by mechanical means, by thermal shock, by pressure alteration, or by ultrasonics. Preferably, the flowable polymer mixture is sheared by mechanical methods in which portions of the melt are caused to
5 flow past other portions of the mixture by use of mechanical means such as stirrers, Banbury® type mixers, Brabender® type mixers, Farrel® continuous mixers, and extruders. Most preferably, the mixture is subjected to multiple shearings. In addition to the increased shear provided by multiple shearing,
10 increased residence time is also provided, which results in improved performance properties. Another procedure employs thermal shock in which shearing is achieved by alternatively raising or lowering the temperature of the mixture causing thermal expansions and resulting in internal stresses which cause
15 the shear. In still other procedures, shear is achieved by sudden pressure changes in pressure alteration methods; by ultrasonic techniques in which cavitation or resonant vibrations which cause portions of the mixture to vibrate or to be excited at different phases and thus subjected to shear. These methods
20 of shearing flowable polymer mixtures and polymer melts are merely representative of useful methods, and any method known in the art for shearing flowable polymer mixtures and polymer melts may be used.

Shearing can be achieved by introducing the polymer
25 pellets at one end of the extruder (single or twin screw) and receiving the sheared polymer at the other end of the extruder. A preferred twin screw extruder is a co-rotating fully intermeshing type, such as the ZSK series manufactured by Werner and Pfleiderer Company. The layered silicate can be fed into the
30 twin screw extruder at the feed throat or at the downstream vent. The preferred method is to feed the layered silicate at the downstream vent, which produces a composite polymer with improved performance properties.

Optionally, an additional processing step can be added, such as solid state polymerization, wherein the compounded pellets are held for several hours at a high temperature below the melting point of the polymer. For example, typical solid state polymerization conditions are heating the solid polymer in the range of about 200 to 240°C for a period of from about two (2) to five (5) hours. Said additional processing step results in an increase in molecular weight and an improvement in toughness, ductility and tensile strength of the nanocomposite.

Another optional processing step can be a heat treatment step, where the composition is heated to improve intercalation of the nylon molecules into the silicate structure. Said heat treatment step is performed by heating the composition at a temperature in the range of about 200 to 240°C for a period of about two (2) to five (5) hours.

Another preferred continuous compounder is the Farrel Continuous Mixer (FCM). For composites using Vydene® 21 nylon, the preferred temperature of the melt is in the range from about 275 to 315°C, with the most preferred range being from about 275 to 295°C.

The polymer melt containing nano-dispersed dissociated silicate material may also be formed by reactive extrusion in which the silicate material is initially dispersed as aggregates or at the nanoscale in a liquid or solid monomer and this monomer is subsequently polymerized in an extruder or the like. Alternatively, the polymer may be granulated and dry mixed with the treated silicate material, and thereafter, the composition may be heated in a mixer until the polymer is melted forming the flowable mixture.

The process to form the nanocomposite is preferably carried out in the absence of air, as for example in the presence of an inert gas, such as argon, neon or nitrogen. The process

can be carried out in a batchwise or discontinuous fashion, as for example, carrying out the process in a sealed container. Alternatively, the process can be carried out in a continuous fashion in a single processing zone, as for example, by use of an extruder, from which air is largely excluded, or in a plurality of such reaction zones in series or in parallel.

In another embodiment of the present invention, the process to prepare a polymer nanocomposite composition comprises forming a first flowable mixture of a polyamide, at least one monomer, and a treated silicate material; dissociating at least 50% but not all of the treated silicate material and polymerizing the monomer. It is to be understood that the polymerization step can occur simultaneously or sequentially with one or more other steps in the process of this embodiment. Preferably, at least one monomer of the third embodiment includes monomers such as ϵ -caprolactam, lauryllactam, and their corresponding lactones.

In yet another embodiment of the present invention, the process to prepare a polymer nanocomposite composition comprises forming a flowable mixture of a polyamide and a treated silicate material; dissociating the at least about 50% but not all of the treated silicate material; and adding an additional amount of said polyamide, most preferably during said dissociating step.

Each of the above embodiments of the process to prepare the polymer nanocomposite composition can be followed by additional steps or treatments, such as solid state polymerization, or additional melt polymerization of the composition by increasing the residence time in the mixer with the removal of water condensation product.

The composition of the present invention can be made into, but is not limited to, the form of a fiber, film or a molded article.

Examples

The following examples are presented to further illustrate the invention and do not limit the scope of the claims in any manner.

- 5 All of the nylons used in the following examples are nylon 6,6. Unless otherwise indicated, the nylon used was nylon h, manufactured by Solutia, Inc, and characterized in the Table of Nylon Types, below. Unless otherwise indicated, all percents are weight percent. The % clay is the total weight of pristine clay
10 in the final composite, be it pristine or pre-treated. Tensile strength and Young's Modulus are measured according to ASTM method D638 and are reported in kpsi and MPa. Flexural modulus is measured according to ASTM method D790 and is reported in kpsi and MPa.
- 15 The runs numbered with a "-C" are control runs.

Table 1 of Clay Types

All of the silicates listed below, unless otherwise identified, are montmorillonites produced by Southern Clay Products Inc. with a clay exchange capacity of about 95. The treatments listed below are ammonium treatments. Items A-H are controls while the items I-AA are examples of quaternary ammonium treated silicates of the present invention.

Item	<u>Ammonium Treatment</u>	<u>MER</u>
10	A untreated B hectorite, untreated C dicyclohexyl D 12-aminolauric acid E dimethyldi(hydrogenated tallow) F dimethylbenzyl hydrogenated tallow G dimethyldi(hydrogenated tallow) H methylbenzyl di(hydrogenated tallow)	-- -- 100 90 140 140 140 130
20	I trimethyl tallow J dimethyldi(hydrogenated tallow) K dimethyldi(hydrogenated tallow) L trimethyl hydrogenated tallow M dimethyl(ethylhexyl)	125 80 85 125
25	hydrogenated tallow N dimethyl(ethylhexyl) hydrogenated tallow, with wetting agent O dimethyl(ethylhexyl) hydrogenated tallow, with wetting agent	90 90 90 90
30	P diethoxymethyl tallow Q dimethyldi(hydrogenated tallow), fine ground clay, with additional processing	90 95 95
35	R octadecylmethyldiethoxy S trimethyl C ₂₂ T dimethyldi(hydrogenated tallow), better dispersing form U dimethyldi(hydrogenated tallow), processed	110 95 95
40	V item U, above, with 1% surfactant W dimethyldi(hydrogenated tallow) X dimethyldi(hydrogenated tallow), fine ground clay	95 95 125 95
45	Y N,N-2-butoxydi(hydrogenated tallow) Z dimethyldi(hydrogenated tallow)	90 95

AA dimethylbenzyl hydrogenated tallow 95

Table 2 of Clay Types

Items GG through NN are examples of montmorillonite, unless otherwise indicated, treated with the blends of more than one quaternary ammonium or of a quaternary ammonium and ammonium of the present invention. Items OO through TT are examples of the tertiary ammonium silicates of the present invention.

<u>Item</u>	<u>Ammonium Treatment</u>	<u>MER</u>
10 GG ¹	80/20 blend of sepiolite and smectite, treated with 75/25 blend of methylbenzyl di(hydrogenated tallow) and dimethyl di(hydrogenated tallow)	45
15 HH	50/50 blend of 2-ethylhexyl, dimethyl hydrogenated tallow and dimethyl di(hydrogenated tallow)	95
II	25/75 blend of 2-ethylhexyl, dimethyl hydrogenated tallow and dimethyl di(hydrogenated tallow)	95
20 JJ	75/25 blend of 2-ethylhexyl, dimethyl hydrogenated tallow and dimethyl di(hydrogenated tallow)	95
KK	10.5/89.5 blend of 12-aminolauric acid and dimethyl di(hydrogenated tallow)	95
25 LL	16/84 blend of 12-aminolauric acid and dimethyl di(hydrogenated tallow),	95
MM	5/95 blend of 12-aminolauric acid and dimethyl di(hydrogenated tallow)	95
30 NN	16/84 blend of 12-aminolauric acid and dimethyl (ethylhexyl) hydrogenated tallow	95
OO	dimethyl cocoa	95
PP	dimethyl hydrogenated tallow	95
QQ	dimethyl tallow	95
35 RR	2-ethylhexyl methyl hydrogenated tallow	95
SS	dimethyl hydrogenated tallow	95
TT	dihydroxyethyl octadecyl	125

¹ Patent Pending

Table of Nylon Types

<u>Nylon</u>	<u>Amine Ends</u>	<u>Acid Ends</u>	<u>Amine/Acid</u>	<u>M_w</u> (1000 D)
a	55	60	0.92	35
5 b	35	60	0.58	42
c	40	40	1.00	50
d	15	50	0.30	62
e	80	50	1.60	31
f	125	70	1.79	21
10 g	31	60	0.52	44
h	45	70	0.64	35

The amine ends and the acid ends are the equivalents of unreacted amine and acid functional groups on the nylon. The M_w is the weight average molecular weight as measured in Daltons.

15

In Table 1, composites of four (4) different types of treated clay are shown. The control examples using clays not treated with ammoniums of the present invention show a general decrease in tensile strength when compared to the preceding (i.e. comparable) sample containing no clay (i.e., comparing 2-C, 3-C and 4-C to 1-C and comparing 6-C, 7-C and 8-C to 5-C), with the exception of control example 3-C which shows no change in tensile strength when compared to 1-C.

Runs 1-C through 4-C were processed with a ZSK twin screw extruder, and runs 5-C through 8-C were processed with a FCM mixer.

Table 1
Control Runs
(Clays not treated with Quaternary Amines)

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
1-C	--	0	11.6 (80.3)	412 (2860)	425 (2940)	286
2-C	A	3.6	11.2 (77.7)	449 (3110)	463 (3210)	285
3-C	A	6.5	11.6 (80.7)	466 (3230)	463 (3210)	286
4-C	B	7.1	11.3 (78.1)	481 (3330)	482 (3340)	286
5-C	--	0	11.6 (80.7)	445 (3080)	436 (3020)	280
6-C	C	2.9	9.65 (66.9)	494 (3420)	481 (3330)	291
7-C	C	8.8	8.08 (56.0)	576 (3990)	568 (3940)	293
8-C	D	4.8	9.11 (63.1)	580 (4020)	550 (3810)	285

In Table 2, composites of four different treated quaternary ammonium-treated clays with a MER exceeding 125 are shown. The composites were processed using a ZSK mixer. All of the control examples show a decrease in tensile strength when
5 compared to the preceding (corresponding) sample without clay.

Table 2
Control Runs
(Treated Clays with MER's Exceeding 125)

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
9-C	--	0	11.3 (78.3)	417 (2980)	432 (2990)	286
10-C	G	13.3	9.78 (67.8)	610 (4230)	613 (4250)	286
11-C	--	0	11.2 (77.4)	423 (2930)	416 (2880)	277
12-C	E	4.2	10.6 (73.4)	520 (3600)	455 (3150)	277
13-C	E	4.4	10.6 (73.2)	500 (3460)	471 (3260)	279
14-C	E	9.6	9.48 (65.7)	553 (3830)	501 (3470)	285
15-C	--	0	11.3 (78.4)	430 (2980)	445 (3080)	286
16-C	H	11.6	7.47 (51.8)	582 (4030)	573 (3970)	291
17-C	H	11.8	7.73 (53.6)	561 (3890)	549 (3760)	285
18-C	H	6.0	10.6 (73.1)	523 (3620)	516 (3580)	288
19-C	H	11.8	5.41 (37.5)	593 (4110)	571 (3960)	295
20-C	H	6.0	10.5 (72.6)	510 (3530)	507 (3510)	283
21-C	H	8.9	10.3 (71.1)	555 (3850)	541 (3750)	289
22-C	--	0	12.0 (82.9)	424 (2940)	432 (3850)	285
23-C	F	7.3	11.2	557	555	287

In Table 3, composites prepared from thirteen (13) different quaternary ammonium-treated clay processed with a FCM compounder are shown. All of the composites except 35, 36 and 47, show an increase in tensile modulus and flexural modulus without a decrease in tensile strength when compared with nylon without the treated clay. However, taking into account the standard deviation of samples 35, 36 and 47, the samples could provide a tensile strength equal to or higher than that of their controls.

Table 3
Quaternary Ammonium Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
24-C	--	0	11.6 (80.7)	445 (3080)	436 (3020)	280
25	P	3.0	12.5 (86.3)	580 (4020)	539 (3740)	292
26	P	5.8	11.6 (80.7)	657 (4550)	633 (4390)	293
27	S	3.3	12.1 (84.0)	524 (3630)	524 (3630)	291
28	T	5.4	12.0 (83.2)	596 (4130)	558 (3870)	288
29-C	--	0	11.4 (78.7)	443 (3070)	425 (2940)	285
30	I	1.8	11.6 (80.4)	509 (3530)	470 (3260)	286
31	R	0.6	12.4 (85.9)	482 (3340)	457 (3170)	286
32	M	0.6	11.5 (79.8)	457 (3170)	438 (3040)	285
33	N	1.6	12.1 (83.9)	504 (3490)	474 (3280)	286
34-C	--	0	11.5 (79.5)	463 (3190)	429 (2960)	286
35	J	1.0	10.3 ¹ 453 (71.5)	448 (3140)	284 (3100)	
36	J	3.3	11.3 ² 500 (78.5)	496 (3460)	288 (3440)	
37	L	2.5	12.0 (83.4)	525 (3640)	502 (3480)	284
38	L	3.3	11.8 (81.6)	535 (3710)	516 (3580)	286
¹ ±1.44		² ±0.98				

Table 3, Continued
Quaternary Ammonium Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
39	W	1.7	11.8 (81.8)	462 (3200)	474 (3280)	285
40	W	4.7	11.7 (80.9)	523 (3620)	507 (3510)	286
41	K	0.8	11.7 (80.9)	449 (3110)	450 (3120)	285
42	K	2.3	11.8 (81.8)	474 (3280)	476 (3300)	286
43	Y	2.6	11.7 (81.1)	476 (3300)	482 (3340)	285
44	Y	4.7	12.1 (83.9)	546 (3780)	525 (3640)	285
45-C	--	0	11.5 (79.8)	469 (3250)	428 (2970)	281
46	Q	1.4	12.1 (83.6)	513 (3560)	478 (3310)	291
47	Q	5.7	11.4 ¹ (79.3)	614 ¹ (4260)	559 ¹ (3870)	294

¹ ± 0.4

In Table 4, composites are prepared from eight (8) different quaternary ammonium-treated clay processed with a ZSK twin screw extruder are shown. All of the composites show an increase in tensile modulus and flexural modulus without a
5 decrease in tensile strength when compared to samples without treated clay.

Table 4
Quaternary Ammonium Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
48-C	--	0	11.5 (79.4)	446 (3090)	431 (2990)	285
49	M	1.7	11.7 (81.1)	480 (3330)	476 (3300)	286
50	M	4.1	12.0 (83.2)	543 (3760)	532 (3690)	287
51	N	2.4	11.6 (80.3)	484 (3350)	502 (3480)	287
52	N	4.1	11.5 (79.7)	508 (3520)	470 (3260)	287
53	O	1.9	11.6 (80.1)	462 (3200)	470 (3260)	287
54	O	4.0	11.5 (79.3)	488 (3380)	494 (3420)	287
55-C	--	0	12.0 (82.9)	424 (2940)	432 (2990)	285
56	U	7.5	12.1 (83.6)	525 (3640)	520 (3600)	286
57	V	7.0	12.1 (84.0)	516 (3580)	521 (3610)	285

Table 4, Continued
Quaternary Ammonium Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
58-C	--	0	11.5 (80.0)	445 (3080)	431 (2990)	287
59	U	2.1	11.8 (82.1)	475 (3290)	483 (3350)	287
60	U	5.2	11.6 (80.1)	560 (4020)	540 (3740)	287
61	U ¹	5.3	12.1 (83.4)	575 (3970)	555 (3830)	287
62	U ²	5.3	12.3 (84.8)	564 (3890)	539 (3720)	288
63-C	--	0	11.31 (78.4)	430 (3080)	445 (3080)	286
64	X	4.9	11.76 (81.5)	606 (4200)	568 (3940)	288
65	X	6.4	11.27 (78.1)	573 (3970)	604 (4190)	295
66-C	--	0	11.55 (79.7)	423 (2930)	424 (2930)	286
67	Q	3.0	11.63 (80.6)	487 (3380)	456 (3160)	286
68	Q	6.5	11.61 (80.5)	514 (3560)	515 (3570)	288
69	Q	11.1	11.60 (80.4)	659 (4570)	579 (4010)	290
70	Q	11.4	12.47 (86.4)	782 (5420)	622 (4310)	289

¹ Second pass of example 60 through ZSK mixer.
² Third pass of example 60 through ZSK mixer.

Table 4, Continued
Quaternary Ammonium Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
71-C	--	0	11.3 (77.9)	459 (3170)	446 (3080)	281
72	AA	3.8	12.5 (86.2)	552 (3810)	487 (3360)	282
73	AA	6.8	12.2 (84.1)	562 (3880)	520 (3590)	282
74	AA	8.9	11.5 (79.3)	612 (4220)	553 (3810)	282

In Table 5, the following four (4) nylon 6,6 products were used to prepare composites: nylon d, nylon c, nylon b, nylon h, shown in the Table of Nylon Types. The nylons are presented above in order of decreasing average molecular weight. The
5 composites were processed using a ZSK twin screw extruder.

All composites show an increase in tensile modulus and flexural modulus without a decrease in tensile strength when compared to samples without treated clay.

Table 5
Varying Nylon Type

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Nylon Type	Melt Temp. (°C)
75-C	--	0	11.3 (78.4)	427 (2960)	430 (2980)	d	291
76	Q	7.3	12.4 (86.0)	600 (4160)	559 (3870)	d	290
77-C	--	0	11.6 (80.4)	402 (2790)	435 (3010)	c	289
78	Q	7.6	12.6 (87.3)	640 (4440)	577 (4000)	c	289
79-C	--	0	11.6 (80.4)	405 (2810)	434 (3010)	b	288
80	Q	7.3	12.0 (83.2)	569 (3940)	546 (3780)	b	289
81-C	--	0	11.1 (76.9)	435 (3010)	430 (2980)	h	288
82	Q	7.1	11.6 (80.4)	556 (3050)	528 (3680)	h	287

- In Table 6, composites using polymer blends of nylon h and nylon b were made. One blend, example 85, was made by preparing a clay concentrate in nylon h, such as control sample 83-C, and then blending the concentrate with a second polymer, such as b.
- 5 The second blend, example 86, was made by preparing a clay concentrate of nylon b, and blending in the nylon h. The composites were processed using a ZSK twin screw extruder.

Table 6
Varying Nylon Blend

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Nylon Type	Melt Temp. (°C)
83-C	Q	20.1	7.77 (53.8)	824 (5710)	722 (5000)	h	280
84	Q	7.1	11.9 (82.5)	612 (4240)	547 (3790)	h	281
85	Q	7.3	12.2 (84.5)	593 (4110)	549 (3800)	b/h ¹	281
86	Q	5.9	12.3 (85.2)	613 (4250)	529 (3670)	h/b ²	281
87	Q	6.3	12.3 (85.2)	588 (4070)	540 (3740)	b	282

¹The weight ratio of nylon blend b/h was 70/30.

²The weight ratio of nylon blend h/b was 70/30.

In Table 7, a concentrate of the treated clay and a polymer other than a polyamide is let down, or diluted with the nylon h. The controls are a mixture of the polymer neat and nylon h.

Table 7
Clay/Other Polymer Concentrate Let Down With Nylon

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Other Polymer (%)	Melt Temp. (°C)
88-C	--	0	9.49 (65.7)	372 (2580)	322 (2230)	12.7 ¹ 288	
89	Z	6.5	9.96 (68.9)	452 (3130)	411 (2840)	12.7 ¹ 287	
90-C	--	0	10.4 (71.6)	393 (2720)	370 (2560)	7.0 ¹	287
91	Z	7.1	10.5 (72.8)	472 (3260)	451 (3120)	7.0 ¹	283
92-C	--	0	8.75 (60.6)	352 (2440)	319 (2210)	15.4 ² 288	
93	Z	7.4	9.67 (66.9)	436 (3020)	437 (3020)	15.4 ² 281	
94-C	--	0	9.52 (65.9)	380 (2630)	354 (2450)	9.7 ²	287
95	Z	7.2	10.5 (72.8)	515 (3560)	471 (3260)	9.7 ²	281

¹The other polymer used was Iotek 971 ionomer.

²The other polymer used was ATX 320 acid terpolymer.

The runs in Table 8 vary the feed points for processing the nylon with the treated clay. The clay was fed into the ZSK twin screw extruder at the throat or downstream of the throat. The nylon used was a copolymer of 80% nylon 6,6 and 20% nylon 6.

Table 8
Varying Feed Point of Nylon for Processing

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
96-C	--	0	10.5 (72.8)	376 (2600)	286 (1980)	251
97	Q	5.4	10.7 (73.4)	468 (3240)	391 (2710)	251 ¹
98	Q	5.5	10.8 (74.5)	489 (3370)	370 (2560)	249 ²
99	Q	2.9	10.5 (72.7)	467 (3230)	378 (2620)	250 ³
100	Q	3.4	10.9 (75.2)	490 (3390)	377 (2610)	250 ⁴
101	Q	4.7	10.6 (73.6)	500 (3460)	375 (2600)	250 ⁵
102	Q	4.8	10.8 (75.1)	521 (3620)	406 (2810)	250 ⁶
103	Q	3.8	10.6 (73.4)	463 (3200)	350 (2420)	256 ⁷
104	Q	4.2	10.8 (74.7)	490 (3390)	359 (2480)	250 ⁸

¹ Nylon fed in throat of ZSK twin screw extruder.

² Second pass of run 97.

³ Nylon fed downstream of throat of extruder.

⁴ Second pass of run 99.

⁵ Nylon fed downstream of throat of extruder.

⁶ Second pass of run 101.

⁷ Nylon fed in throat of extruder.

⁸ Second pass of run 103.

In Table 9, composites are prepared from eight (8) different quaternary ammonium/ammonium blend-treated silicates. The composites are processed using a ZSK twin screw extruder. Taking into account the standard deviations of the tensile strength measurements, all of the samples show an increase in tensile modulus and flex modulus without a decrease in tensile strength. Samples 125 through 135 show the effect of varying the nylon type.

Table 9
Ammonium Blend-Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
105-C*	--	0	11.4 (78.6)	455 (3140)	450 (3100)	259
106*	GG	5.6	13.7 (94.5)	596 (4110)	578 (3990)	263
107-C	--	0	11.5 (79.3)	463 (3190)	429 (2960)	286
108	HH	1.3	11.8 (81.4)	476 (3280)	472 (3260)	285
109	HH	5.2	11.4 ¹ 552 (78.7)	545 (3810)	286 (3760)	
110	II	2.3	12.0 (82.8)	465 (3210)	429 (2960)	286
111	II	5.6	11.8 (81.4)	560 (3860)	545 (3760)	285
112	JJ	2.0	11.9 (82.1)	470 (3240)	483 (3330)	285
113	JJ	4.3	11.5 (79.3)	542 (3740)	537 (3700)	286

*Runs 105 and 106 use nylon f.
¹ Standard deviation of ± 0.85 .

Table 9, Continued
Ammonium Blend-Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
114-C	--	0	11.2 (77.2)	411 (2830)	405 (2790)	287
115	KK	2.8	11.5 (79.3)	470 (3240)	475 (3280)	287
116	KK	6.2	10.9 ¹ 494 (75.2)	536 (3410)	288 (3700)	
117	LL	3.4	11.6 (80.0)	500 (3450)	510 (3520)	288
118	LL	6.7	11.0 ² 544 (75.9)	542 (3750)	288 (3740)	
119	MM	3.2	11.5 (79.3)	480 (3310)	497 (3430)	287
120	MM	6.5	11.0 ³ 529 (75.9)	540 (3670)	288 (3720)	
121-C	--	0	11.6 (80.0)	427 (2940)	466 (3210)	282
122	NN	3.5	12.6 (86.9)	522 (3600)	568 (3920)	282
123	NN	6.5	12.6 (86.9)	572 (3940)	623 (4300)	282
124	NN	8.4	11.3 ⁴ 650 (77.9)	664 (4480)	283 (4580)	

¹ Standard Deviation of ± 1.22

² Standard Deviation of ± 0.24

³ Standard Deviation of ± 0.49

⁴ Standard Deviation of ± 0.60

Table 9, Continued
Ammonium Blend-Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
125-C ¹	--	0	11.7 (80.7)	488 (3370)	481 (3320)	268
126 ¹	NN	8.1	11.9 (82.1)	640 (4410)	598 (4120)	265
127-C ²	--	0	11.4 (78.6)	482 (3320)	454 (3130)	285
128 ²	NN	8.1	11.7 (80.7)	658 (4540)	618 (4260)	315
129-C ³	--	0	11.4 (78.6)	434 (2990)	441 (3040)	262
130 ³	NN	1.7	12.1 (83.4)	491 (3390)	506 (3490)	270
131 ³	NN	4.0	12.8 (88.3)	567 (3910)	557 (3840)	276
132-C ⁴	--	0	11.8 (81.4)	434 (2990)	439 (3030)	269
133 ⁴	NN	2.2	12.1 (83.4)	480 (3310)	509 (3510)	276
134 ⁴	NN	4.3	12.5 (86.2)	580 (4000)	557 (3840)	282
135 ⁴	NN	6.8	12.4 (85.5)	635 (4380)	643 (4430)	286

- ¹ Samples use nylon a.
² Samples use nylon c.
³ Samples use nylon a.
⁴ Samples use nylon e.

In Table 10, composites are prepared from six (6) different tertiary ammonium-treated silicates. The composites are processed using a ZSK twin screw extruder. Taking into effect the standard deviation of the tensile strength

5 measurements, all of the samples show an increase in tensile modulus and flex modulus without a decrease in tensile strength.

Table 10
Tertiary Ammonium Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
136-C	--	0	12.1 (83.4)	443 (3060)	456 (3140)	296
137	OO	5.4	13.0 (89.7)	591 (4080)	568 (3920)	297
138	PP	4.9	12.9 (89.0)	588 (4060)	545 (3760)	297
139	QQ	4.1	12.8 (88.3)	573 (3950)	549 (3790)	296
140	RR	4.4	12.4 (85.5)	533 (3680)	518 (3570)	297
141	SS	3.1	11.9 ¹ (82.1)	488 (3370)	296 (3440)	
142-C	--	0	11.6 (80.0)	445 (3070)	436 (3010)	280
143	TT	2.7	12.2 (84.1)	508 (3500)	497 (3430)	283
144	TT	6.2	12.3 (84.8)	587 (4050)	571 (3940)	287

¹ Standard Deviation of ± 1.1

In Table 11, samples 147, 150, 152, 154 and 156 are subjected to solid state polymerization. A dramatic improvement is noted in the tensile strength and elongation.

Table 11
Process Variations

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	% Elongation	Melt Temp. (°C)
145-C	--	0	11.7 (80.7)	488 (3370)	481 (3320)	29.4	268
146	NN	8.1	11.9 (82.1)	640 (4410)	598 (4120)	2.5	265
147 ¹	NN	8.1	14.2 (97.9)	689 (4750)	630 (4340)	3.2	265
148-C	--	0	11.4 (78.6)	482 (3320)	454 (3130)	33.8	285
149	NN	8.1	11.7 (80.7)	658 (4540)	618 (4260)	2.1	315
150 ¹	NN	8.1	13.9 (95.9)	681 (4700)	663 (4570)	2.9	315
151-C	--	0	11.4 (78.6)	421 (2910)	430 (2980)	38.8	275
152 ¹ -C	--	0	11.5 (79.7)	428 (2970)	446 (3090)	40.4	275
153	NN	5.1	13.6 (94.2)	620 (4300)	569 (3940)	12.7	--
154 ¹	NN	5.1	13.7 (94.9)	536 (3710)	574 (3980)	10.7	--
155 ²	NN	3.9	12.7 (88.0)	560 (3880)	538 (3730)	5.8	280
156 ^{1,2}	NN	3.9	12.9 (89.4)	524 (3630)	513 (3560)	20.5	280

¹ Subjected to solid state polymerization at about 220°C for about 3 to 4 h.

² Stabilized with 0.25% Irganox LC21FF stabilizer sold by Ciba-Geigy Co.

Samples 145 to 147 and 151 to 156 use nylon a.

Samples 148 to 150 use nylon c.

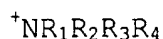
Claims:

1. A polymer nanocomposite composition comprising:

(1) a polyamide, and

5 (2) treated silicate, wherein

said silicate material comprises silicate material treated with
at least one ammonium ion of the formula:



wherein R_1 , R_2 , R_3 and R_4 are independently selected from a
10 group consisting of a saturated or unsaturated C_1 to C_{22}
hydrocarbon, substituted hydrocarbon and branched hydrocarbon, or
where R_1 and R_2 form a N,N-cyclic ether; wherein,
optionally, one of R_1 , R_2 , R_3 and R_4 is hydrogen;

wherein the MER of the treated silicate is from about 10
15 milliequivalents/100 g below the cation exchange capacity of the
untreated silicate to about 30 milliequivalents/100 g above the
cation exchange capacity of the untreated silicate; and

wherein the nanocomposite polyamide material demonstrates,
when tested, an improvement in tensile modulus and flexural
20 modulus, without a substantial decrease in tensile strength, when
compared with that of the polyamide without the layered silicate.

2. The composition of claim 1, wherein the polyamide is
selected from the group consisting of nylon 6, nylon 6,6, nylon

4,6, nylon 6,9, nylon 6,10, nylon 6,12, nylon 11, nylon 12, amorphous nylons, aromatic nylons and their copolymers.

3. The composition of claim 1, wherein the polyamide is nylon 6,6 and its copolymers.

5 4. The composition of claim 1, wherein said treated silicate is a layered silicate selected from the group consisting of montmorillonite, nontronite, beidellite, volkonskoite, natural or synthetic hectorite, saponite, sauconite, magadite and kenyaite.

10 5. The composition of claim 1, wherein said treated silicate is a fibrous, chain-like silicates selected from the group consisting of chain-like minerals, sepiolite and attapulgite.

15 6. The composition of claim 1, wherein the composition includes at least one surfactant, nucleating agent, coupling agent, filler, plasticizer, impact modifier, chain extender, compatibilizer, colorant, lubricant, antistatic agent, pigment or fire retardant.

20 7. The composition of claim 6, wherein the coupling agent is a silane.

8. The composition of claim 7, wherein the silane coupling agent is gamma-aminopropyltriethoxysilane.

9. The composition of claim 8, wherein the silane coupling agent concentration in the polymer composite is in the range of about 0.5 to 5 weight % of the layered silicate.

10. The composition of claim 1, wherein R_1 is selected from the group consisting of hydrogenated tallow, unsaturated tallow or a hydrocarbon having at least 6 carbons and R_2 , R_3 and R_4 independently have from one to twelve carbons.

11. The composition of claim 1, wherein the ammonium ions are quaternary ammonium ions selected from the group consisting of dimethyldi(hydrogenated tallow) ammonium, dimethylbenzyl hydrogenated tallow ammonium, dimethyl(ethylhexyl) hydrogenated tallow ammonium, trimethyl hydrogenated tallow ammonium, methylbenzyldi(hydrogenated tallow) ammonium, N,N-2-cyclobutoxydi(hydrogenated tallow) ammonium, trimethyl tallow ammonium, methyldihydroxyethyl tallow ammonium and octadecylmethyldihydroxyethyl ammonium, or a mixture thereof.

12. The composition of claim 1, wherein the ammonium ions are quaternary ammonium ions selected from the group consisting of dimethyldi(hydrogenated tallow) ammonium, dimethyl(ethylhexyl) hydrogenated tallow ammonium, dimethylbenzyl hydrogenated tallow ammonium, methyldihydroxyethyl tallow ammonium, or a mixture thereof.

13. The composition of claim 1, wherein the composition has a concentration of treated silicate of from about 0.1 to about 12.0 weight % of the composite.

14. The composition of claim 1, wherein the composition
5 has a concentration of treated layered silicate of from about 0.5 to about 6.0 weight % of the composite.

15. The composition according to claim 1, wherein said composition comprises at least one other polymer.

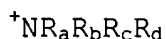
16. The composition according to claim 15, wherein said
10 at least one other polymer comprises poly(phenylene oxide) or poly(phenylene ether).

17. The composition according to claim 1, wherein said polyamide has a weight average molecular weight of at least about 40,000 D.

15 18. The composition according to claim 15, wherein said other polymer comprises polyethyleneoxide, polycarbonate, polyethylene, polypropylene, poly(styrene-acrylonitrile), poly(acrylonitrile-butadiene-styrene), poly(ethylene terephthalate), poly(butylene terephthalate), poly(trimethylene
20 terephthalate), poly(ethylene naphthalate), poly(ethylene terephthalate-co-cyclohexane dimethanol terephthalate), polysulphone, poly(phenylene oxide) or poly(phenylene ether), poly(hydroxybenzoic acid-co-ethylene terephthalate), poly(hydroxybenzoic acid-co-hydroxynaphthenic acid),

poly(esteramide), poly(etherimide), poly(phenylene sulfide), and poly(phenylene terephthalamide).

19. The composition according to claim 1, wherein said treated silicate particles are treated with a mixture of one
5 or more quaternary ammonium ions with an ammonium ion of the formula



wherein at least one of R_a , R_b and R_c is hydrogen (H) and R_d is selected from a group consisting of a saturated or
10 unsaturated C_1 to C_{22} hydrocarbon, substituted hydrocarbon and branched hydrocarbon, or where R_1 and R_2 form a N,N-cyclic ether.

20. The composition according to claim 19, wherein R_d includes a carboxylic acid moiety.

21. The composition according to claim 19, wherein said
15 mixture includes at least one of dimethyldi(hydrogenated tallow) ammonium, methylhydroxyethyl tallow ammonium and/or dimethyl(ethylhexyl) hydrogenated tallow ammonium in combination with 12-aminolauric acid ammonium.

22. The composition according to claim 1, wherein said
20 layered silicate particles are treated with azine cationic dyes.

23. The composition according to claim 22, wherein the said cationic dyes comprise nigrosines or anthracenes.

24. The composition according to claim 6, wherein the said filler comprises carbon fiber, glass fiber, kaolin clay, wollastonite or talc.

25. The composition according to claim 6, wherein said
5 compatibilizer comprises at least one acid-modified hydrocarbon polymer.

26. The composition according to claim 6, wherein said compatibilizer comprises maleic anhydride-grafted polyethylene, maleic anhydride-grafted polypropylene, or maleic anhydride-
10 grafted ethylene-butylene-styrene block copolymer.

27. The composition according to claim 6, wherein said lubricant comprises at least one alkyl amine, stearamide, or di- or tri- aluminum stearate.

28. The composition according to claim 6, wherein said
15 impact modifier comprises ethylene-propylene rubber, ethylene-propylene diene rubber, methacrylate-butadiene-styrene (with core-shell morphology), poly(butylacrylate) with or without carboxyl modification, poly(ethylene acrylate), poly(ethylene methylacrylate), poly(ethylene acrylic acid), poly(ethylene
20 acrylate) ionomers, poly(ethylene methacrylate acrylic acid) terpolymer, poly(styrene-butadiene) block copolymers, poly(styrene-butadiene-styrene) block terpolymers, poly(styrene-ethylene/butylene-styrene) block terpolymers and poly(styrene-ethylene/butylene-styrene carboxylate) block terpolymers.

29. The composition according to claim 1, wherein said composition comprises a composite in which the crystalline regions of the polyamide are less than 1.0 μm .

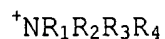
30. The composition according to claim 1, wherein said
5 composition is in the form of a fiber, film or a molded article.

31. A process to prepare a polyamide nanocomposite composition comprising

(1) forming a flowable mixture of a polyamide and a treated silicate material;

10 (2) dissociating at least about 50% but not all of said treated silicate material to form the nanocomposite composition;

wherein the treated silicate comprises a silicate material treated with at least one ammonium ion of the formula:



15 wherein R_1 , R_2 , R_3 and R_4 are independently selected from a group consisting of a saturated or unsaturated C_1 to C_{22} hydrocarbon, substituted hydrocarbon and branched hydrocarbon, or where R_1 and R_2 form a N,N-cyclic ether; wherein, optionally, one of R_1 , R_2 , R_3 and R_4 is hydrogen;

20 wherein the MER of the treated silicate is from about 10 milliequivalents/100 g below the cation exchange capacity of the untreated silicate to about 30 milliequivalents/100 g above the cation exchange capacity of the untreated silicate; and

wherein the nanocomposite polyamide material demonstrates, when tested, an improvement in tensile modulus and flexural modulus, without a decrease in tensile strength, when compared with that of the polyamide without the layered silicate.

5 32. The process of claim 31, wherein the polyamide is selected from the group consisting of nylon 6, nylon 6,6, nylon 4,6, nylon 6,9, nylon 6,10, nylon 6,12, nylon 11, nylon 12, amorphous nylons, aromatic nylons and their copolymers.

10 33. The process of claim 31, wherein the silicate is selected from the group consisting of montmorillonite, nontronite, beidellite, volkonskoite, natural or synthetic hectorite, sepiolite, saponite, sauconite, magadite, and kenyaite.

15 34. The process of claim 31, wherein the composition includes at least one surfactant, nucleating agent, coupling agent, filler, plasticizer, impact modifier, chain extender, compatibilizer, colorant, mold release lubricant, antistatic agent, pigment or fire retardant.

20 35. The process of claim 34, wherein the coupling agent is a silane.

 36. The process of claim 35, wherein the silane coupling agent is gamma-aminopropyltriethoxysilane.

37. The process of claim 35, wherein the silane coupling agent concentration in the polymer composite in the range of about 0.5 to 5 weight % of the layered silicate.

38. The process of claim 31, wherein R_1 is selected from the group consisting of hydrogenated tallow, unsaturated tallow or a hydrocarbon having at least 6 carbons and R_2 , R_3 and R_4 independently have from one to twelve carbons.

39. The process of claim 31, wherein the ammonium ion is a quaternary ammonium ion selected from the group consisting of dimethyldi(hydrogenated tallow) ammonium, dimethylbenzyl hydrogenated tallow ammonium, dimethyl(ethylhexyl) hydrogenated tallow ammonium, trimethyl hydrogenated tallow ammonium, methylbenzyldi(hydrogenated tallow) ammonium, methylhydroxyethyl tallow ammonium, and N,N-2-cyclobutoxydi(hydrogenated tallow) ammonium.

40. The process of claim 31, wherein the composition has a concentration of treated layered silicate of from about 0.1 to about 12.0 weight % of the composite.

41. The process of claim 31, wherein the composition has a concentration of treated layered silicate of from about 0.5 to about 6.0 weight % of the composite.

42. The process of claim 31, wherein the treated silicate is dissociated by a method selected from the group consisting of

mechanical means, thermal shock, pressure alteration, or ultrasonics.

43. The process of claim 42, wherein the mechanical means is selected from the group consisting of stirrers, Banbury® type mixers, Brabender® type mixers, Farrel® continuous mixers, and extruders.

44. The process of claim 43, wherein the extruders are selected from the group consisting of single screw and twin screw.

10 45. The process of claim 44, wherein the twin screw extruder is of the co-rotating fully intermeshing type.

46. The process of claim 42, wherein said flowable mixture is subjected to multiple of said dissociating methods.

15 47. The process of claim 31, wherein said forming step includes mixing said polyamide with a treated silicate containing concentrate, said concentrate including said treated silicate and a carrier polymer.

20 48. The process of claim 47, wherein said carrier polymer comprises polyamide, ethylene-propylene rubber, ethylene-propylene diene rubber, ethylene-ethylacrylate, ethylene-ethylmethacrylate or ethylene methacrylate.

49. The process of claim 48, wherein the polyamide carrier polymer is selected from the group consisting of nylon 6, nylon 6,6, nylon 4,6, nylon 6,9, nylon 6,10, nylon 6,12, nylon

11, nylon 12, amorphous nylons, aromatic nylons and their copolymers.

50. The process of claim 47, wherein said carrier polymer is of a different weight average molecular weight than
5 said polyamide in said flowable mixture.

51. The process of claim 47, wherein said carrier polymer is a polymer other than a polyamide.

52. The process of claim 47, wherein said carrier polymer has a weight average molecular weight of 10,000 to 40,000 D.

10 53. The process of claim 31, wherein said flowable mixture further comprises a monomer.

54. The process of claim 53, wherein said monomer comprises ϵ -caprolactam, lauryllactam, or their corresponding lactones.

15 55. The process of claim 53, wherein said process further comprises polymerizing said monomer.

56. The process of claim 31, further comprising adding additional amount of said polyamide to said flowable mixture during said dissociating step.

20 57. The process of claim 31 further comprising solid state polymerization or additional melt polymerization of said polyamide.

58. The process of claim 57, wherein the solid state polymerization involves heating the polyamide to a temperature in

the range of about 200 to 240°C for a period of about 2 to 5 hours.

59. The process of claim 31 further comprising heat treating the composition to a temperature in the range of about 200 to 240°C for a period of about 2 to 5 hours, wherein such heat treatment can lead to solid state polymerization or improved intercalation of the polyamide molecules into the silicate material.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/02768

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C08J 5/10; C08K 3/34; C08L 77/00

US CL :524/445, 448, 449, 442, 789; 523/204, 216

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/445, 448, 449, 442, 789; 523/204, 216

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US A, 5,514,734 (MAXWELL et al.) 07 May 1996, entire document.	1-59
Y	US A, 4,889,885 (USUKI et al.) 26 December 1989, entire document.	1-9,13-20, 22-37,40-59
A	US A, 5,102,948 (DEGUCHI et al.) 07 April 1992	1-59



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

22 MAY 1998

Date of mailing of the international search report

19 JUN 1998

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